

Alternating spin-orbital order in tetragonal Sr_2VO_4

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(Dated: November 4, 2011)

Considering spin-orbit coupling, the tetragonal crystal-field, and all relevant superexchange processes including quantum interference, we derive expressions for the energy levels of the vanadium ions in tetragonal Sr_2VO_4 . The used parameters of the model Hamiltonian allow to describe well the excitation spectra observed in neutron scattering and optical experiments at low temperatures. The free energy exhibits a minimum which corresponds to a novel alternating spin-orbital order with strong thermal fluctuation of the orbital mixing parameter.

PACS numbers: 78.20.-e, 78.40.-q, 71.70.Ej

In many transition-metal compounds the orbital degrees of freedom play a decisive role in determining the ground-state properties of materials such as manganites titanates, or vanadates.¹ When contributions of the orbital moment and spin-orbit coupling are not negligible a separation between spin and orbital degrees of freedom is not adequate anymore and the system is better described by an effective total angular momentum.^{2,3} If spin-orbit coupling competes with electron-phonon or exchange interactions even strong fluctuation regimes can arise.⁴⁻⁶

The system investigated here is the layered insulator Sr_2VO_4 with tetragonal symmetry, which early on has come into focus as an isostructural d^1 analogue of La_2CuO_4 .⁷ Consequently, it was suggested that Sr_2VO_4 could become superconducting upon applying chemical pressure by doping or external pressure.^{8,9} While the system could not be driven towards superconductivity, it turned out to be a model system for studying the interplay of orbital-lattice, spin-orbital and superexchange interactions.¹⁰⁻¹³

In tetragonal Sr_2VO_4 with space group I_4/mmm ,^{14,15} the octahedrally coordinated V^{4+} ions occupy a square lattice in the ab -plane (see Fig. 1). The magnetic ground state has been claimed to be antiferromagnetic with transition temperatures in the range 10 - 100 K determined from susceptibility measurements, but long-range order remained evasive on the basis of neutron-diffraction studies.^{14,16,17} Recent studies established the occurrence of a magneto-structural phase transition extending over a temperature range from 94 - 122 K. Both the high-temperature and the low-temperature structure are tetragonal and reportedly coexist within this range.¹¹ Specific heat data revealed two distinct broad maxima occurring at 98 and 127 K mirroring the borders of the two-phase regime.^{18,19}

The disappearance of the high-temperature phase is accompanied by a significant drop in the susceptibility at about 100 K, which has been attributed to the onset

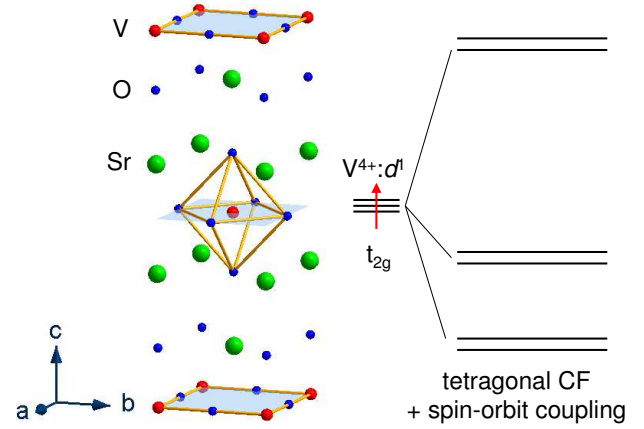


FIG. 1. Left: Unit cell of tetragonal Sr_2VO_4 with symmetry I_4/mmm (Ref. 15) highlighting the VO_2 planes and the octahedral coordination of the V ions. Right: Splitting of the $\text{V}^{4+} t_{2g}$ -levels due to the tetragonal crystal field and spin-orbit coupling.

of long-range AFM and orbital order.¹¹ Theoretically, the ground state of Sr_2VO_4 has been interpreted in terms of stripe-like orbital and collinear AFM spin order,¹⁰ or an ordering of magnetic octupoles.¹² Inelastic neutron scattering revealed two excitations at about 120 meV, which were assigned to the highest lying doublet of the $\text{V}^{4+} t_{2g}$ levels.¹³ Recent optical experiments reported excitations at 31 meV (visible for $T > 80$ K), 36 meV (visible for $T < 120$ K) and a two-peak structure at 100 meV and 108 meV, which remains visible from 13 K to room temperature.¹⁹

To elucidate the nature of the ground state and to understand the observed excitation spectrum we consider the effects of spin-orbit coupling, crystal-field, and superexchange on the energy levels of the vanadium ions. The resulting free energy points towards a novel alternating spin-orbital order in the ground state.

To describe the system of V^{4+} ions we use the Hamil-

tonian $H = H_{si} + H_{ex}$ where H_{ex} describes the exchange coupling of neighbouring ions and H_{si} contains the single-ion contributions in a tetragonal crystal field:

$$H_{si} = D[3l_z^2 - l(l+1)] + \lambda_c l_z s_z + \frac{\lambda_{a,b}}{2}(l_- s_+ + l_+ s_-) \quad (1)$$

Here D denotes the single-ion anisotropy and l the effective angular momentum $l = 1$ of the t_{2g} -orbitals, which we describe using $|1\rangle = -\frac{1}{\sqrt{2}}[d_{yz} + id_{xz}]$, $|-1\rangle = \frac{1}{\sqrt{2}}[d_{yz} - id_{xz}]$, and $|0\rangle = d_{xy}$ as a basis.² Moreover, we use anisotropic spin-orbit coupling constants λ_c and $\lambda_{a,b}$ parallel and perpendicular to the c -direction. Anisotropic spin-orbit coupling can arise due to covalency effects and has been observed in several d^1 systems in octahedral environment.^{2,20}

The superexchange coupling between V ions via oxygen ions in the ab plane is usually described via the corresponding hopping integrals,²¹ which in our case are given by:

$$t_{1,1} = t_{-1,-1} = \frac{1}{2}(t_{xz,xz} + t_{yz,yz}) \quad (2)$$

$$t_{1,-1} = t_{-1,1} = \frac{1}{2}(t_{xz,xz} - t_{yz,yz}) \quad (3)$$

$$t_{0,0} = t_{xy,xy} \quad (4)$$

From the spatial distributions of the d_{xz} and d_{yz} orbitals it is clear that the signs of the transfer integrals $t_{xz,xz}$ and $t_{yz,yz}$ are different and, therefore, $|t_{1,-1}| > |t_{1,1}|$. This observation will allow us to deduce the most likely ordering of the V states in the ground state.

Using the reported crystal structure of Sr_2VO_4 one finds that $D < 0$ and, therefore, the possible ground states of the V^{4+} ions are $|\pm 1, \pm 1/2\rangle$. The antiferromagnetic superexchange coupling (see below) will yield an additional gain in energy when $|-1, \pm 1/2\rangle$ -states are surrounded by $|1, \mp 1/2\rangle$, or vice versa. Then, keeping in mind that the spin-orbit coupling parameters $\lambda_c < 0$, we arrive at a configuration in the ab plane of Sr_2VO_4 where each vanadium ion in the state $|1, 1/2\rangle$ is surrounded by vanadium ions in the $|-1, -1/2\rangle$ state and vice versa. According to the third Hund rule, spin ($s_z = \pm 1/2$) and angular ($l_z = \mp 1$) momentum of the V^{4+} ground state configuration are in opposition. The corresponding combined spin-angular moment per site therefore possesses the peculiarity that the magnetic moment $m_z/\mu_B = 2s_z - \kappa l_z$ is almost completely muted, when the covalency reduction factor κ is close to one.² The resulting ordering scheme can be described as an alternating order of spin and orbital moments on each site.

First, we introduce the superexchange parameters

$$J_a = 4 \frac{t_{xz,xz}^2 + t_{yz,yz}^2}{U} \quad (5)$$

$$J_{int} = -8 \frac{t_{xz,xz} t_{yz,yz}}{U}, \quad (6)$$

where U denotes the onsite Coulomb repulsion. The signs of the transfer integrals $t_{xz,xz}$ and $t_{yz,yz}$ are different

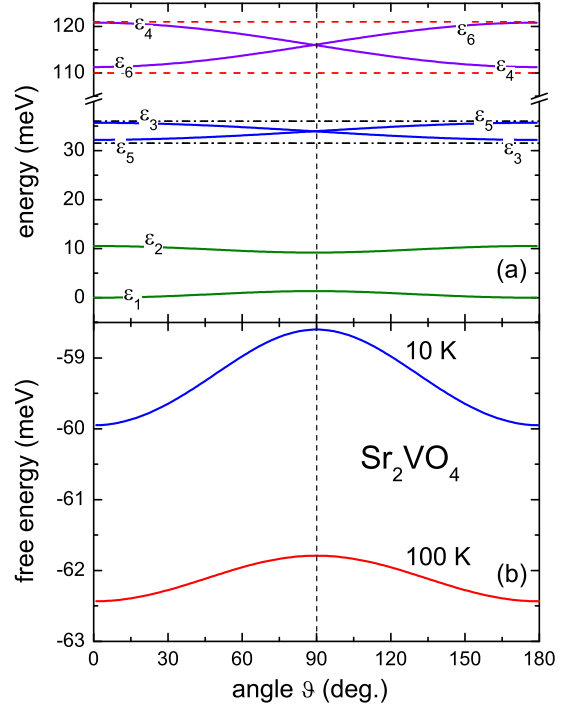


FIG. 2. (a) Calculated energy levels as a function of the orbital mixing angle ϑ using Eqs. (13)-(15) and parameters $\lambda_c = -30$ meV, $\lambda_{ab} = -28$ meV, $D = -33$ meV, $J_a = -15$ meV, $J_f = -9.3$ meV, $J'_f = -0.7$ meV, and $J_{int} = 7.5$ meV. Excitation energies observed by neutron scattering (Ref. 13) and optical spectroscopy (Ref. 19) are shown as dashed and dash-dotted lines, respectively. (b) Free energy as a function of ϑ calculated with the same parameters 10 and 100 K.

and, therefore, the cross term J_{int} is positive. This parameter describes the quantum interference effect in superexchange coupling. The part of the effective exchange Hamiltonian containing these parameters is written as

$$H_{ex}(1) = \frac{J_a}{8} \left(\mathbf{s}_i \mathbf{s}_j - \frac{1}{4} \right) (2l_{iz}^2 l_{jz}^2 + l_{i+}^2 l_{j+}^2 + l_{i-}^2 l_{j-}^2) - \frac{J_{int}}{4} \left(\mathbf{s}_i \mathbf{s}_j - \frac{1}{4} \right) l_{iz} l_{jz}. \quad (7)$$

The ferromagnetic contributions to the superexchange interaction comprise two exchange integrals J_f and J'_f , which for a pair of V ions along the x -axis can be denoted as

$$J_f = J_p - 2 \frac{I_f}{U^2} (t_{xy,xy}^2 + t_{xz,xz}^2) \quad \text{and} \quad (8)$$

$$J'_f = J'_p - 2 \frac{I_f}{U^2} (t_{xz,xz}^2) \quad \text{with} \quad (9)$$

$$I_f = \langle d_{xy}, d_{xz} | \frac{e^2}{r_{12}} | d_{xz}, d_{xy} \rangle.$$

Here I_f is an exchange integral, which can be estimated via Racah parameters as $3B + C = 0.9$ eV and J_p, J'_p correspond to potential exchange contributions. In Eq. (9) the potential exchange parameter J'_p is expected to be

small and will be neglected in the following. Note that J'_f has been called Hunds-coupling parameter in Ref. 12.

In momentum representation for $l = 1$, $s = 1/2$ this part of the exchange Hamiltonian is written as

$$H_{ex}(2_x) = \left(\mathbf{s}_i \mathbf{s}_j + \frac{3}{4} \right) [J_f (-2 + l_{ix}^2 + l_{jx}^2 + l_{iz}^2 l_{jy}^2 + l_{iy}^2 l_{jz}^2) + J'_f (l_{ix}^2 + l_{jx}^2 - 2l_{ix}^2 l_{jx}^2)] \quad (10)$$

The effective Hamiltonian for a pair along the y -axis can be obtained by a permutation of indices $x \rightarrow y$, $y \rightarrow x$. For a detailed discussion of the differences in spin dependent factors of ferro- and antiferromagnetic exchange terms we refer to Ref. 22. Let us consider now a two-sublattice configuration in which each V ion of sublattice i is described by the wave func-

tion $|\vartheta\rangle = \cos \vartheta/2 |1, 1/2\rangle + \sin \vartheta/2 |-1, -1/2\rangle$ with $\vartheta = \vartheta_i$ is surrounded by four V ions of sublattice j with $\vartheta = \vartheta_j$.²³ Using the effective exchange operator $H_{ex} = \sum [H_{ex}(1) + H_{ex}(2_x) + H_{ex}(2_y)]$ and assuming that only the ground states of surrounding V ions are populated we arrive at the following energy spectrum of the vanadium ions:

$$\varepsilon_{1,2} = D + \frac{\lambda_c}{2} - \frac{J_a + J_{int}}{4} + \frac{3J'_f}{2} \pm \frac{1}{4} \left[(J_a + J_{int} + 2J'_f)u^2 + (J_a - J'_f)^2 v^2 \right]^{\frac{1}{2}} \quad (11)$$

$$\begin{aligned} \varepsilon_{3,4} = & -\frac{D}{2} - \frac{\lambda_c}{4} + \frac{J_a - J_{int}}{8}(u - 1) + \frac{J_f}{4}(3 - u) + \frac{3J'_f}{2} \\ & \pm \frac{1}{2} \left[\left(3D - \frac{\lambda_c}{2} + \frac{J_a - J_{int}}{4}(u - 1) - \frac{J_f}{2}(3 - u) + J'_f u \right)^2 + 2\lambda_{a,b}^2 \right]^{\frac{1}{2}} \end{aligned} \quad (12)$$

$$\begin{aligned} \varepsilon_{5,6} = & -\frac{D}{2} - \frac{\lambda_c}{4} - \frac{J_a - J_{int}}{8}(u + 1) + \frac{J_f}{4}(3 + u) + \frac{3J'_f}{2} \\ & \pm \frac{1}{2} \left[\left(3D - \frac{\lambda_c}{2} - \frac{J_a - J_{int}}{4}(u + 1) - \frac{J_f}{2}(3 + u) - J'_f u \right)^2 + 2\lambda_{a,b}^2 \right]^{\frac{1}{2}} \end{aligned} \quad (13)$$

Here we have introduced $u = \cos \vartheta_j$ and $v = \sin \vartheta_j$. From the expressions for $\varepsilon_{3,4}$ and $\varepsilon_{5,6}$ one finds that at $\vartheta = \pm\pi/2$ the excited states are degenerate doublets, i.e. $\varepsilon_3 = \varepsilon_5$ and $\varepsilon_4 = \varepsilon_6$. However, this choice of $\vartheta = \pm\pi/2$ cannot explain the observed splitting of the highest-lying doublet $\varepsilon_{4,6}$ which was observed by neutron scattering and optical spectroscopy.^{13,19}

Now let us turn to the ground state ε_1 . A minimum in energy of this level will occur at $\vartheta = \pm\pi/2$ only if $3|J'_f| > J_{int}$. If $J_{int} > 3|J'_f|$ the minimum will occur at $\vartheta = 0$ or $\vartheta = \pi$. At these angles the excited states are split due to the exchange-molecular field in agreement with experiment.¹³ Using the experimentally observed splitting¹³ of the highest doublet of about 10 meV we estimate the value $|J_f + J'_f| \simeq 10$ meV. Following Imai and coworkers the energy cost for moving a 3d-electron between V ions in Sr_2VO_4 is about $U \simeq 11$ eV and the effective transfer integrals $t_{xz,xz} \simeq -0.2$ eV and $t_{yz,yz} \simeq 0.05$ meV.¹⁰ Therefore, we estimate $J_a \simeq 15$ meV, $J_{int} \simeq$

7.5 meV, $J'_f = -(3B + C)/2U * J_a \simeq -0.7$ meV, and $J_f \simeq -9.3$ meV. The values $D = -33$ meV, $\lambda_c = -30$ meV, and $\lambda_{ab} = -28$ meV are in agreement with conventional estimates.^{2,12} Using these values we plot the energy levels as $\varepsilon_i(\vartheta) - \varepsilon_1(\vartheta = 0, \pi)$ in Fig. 2(a) as a function of the orbital-mixing angle ϑ . Note that $\varepsilon_1(\vartheta)$ is not constant but becomes minimal for $\vartheta = 0, \pi$. The estimated excitation energies $\varepsilon_4 - \varepsilon_1 = 121$ meV, $\varepsilon_6 - \varepsilon_1 = 111$ meV, and $\varepsilon_3 - \varepsilon_1 = 36$ meV for $\vartheta = 0$ (or corresponding values for $\vartheta = \pi$) are in agreement with the transitions observed by optical (dash-dotted lines) and neutron scattering experiments (dashed lines) at low temperatures shown in Fig. 2(a).^{13,19}

In Fig. 2(b) we compare the free energy per vanadium site at 10 and 100 K (close to T_N) as a function of the parameter ϑ using the values for the exchange constants estimated above:

$$F(T, \vartheta) = -k_B T \ln \sum \exp \left(-\frac{\varepsilon_i(\vartheta)}{k_B T} \right) \quad (14)$$

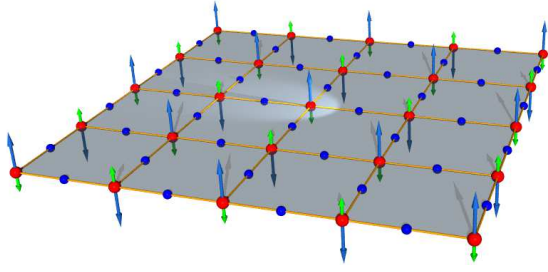


FIG. 3. Sketch of the proposed alternating spin-orbital order in the ab -plane of tetragonal Sr_2VO_4 . Short and long arrows correspond to spin and orbital moments of the V ions, respectively.

There is a minimum at $\vartheta = 0$ and $\vartheta = \pm\pi$ in both cases and the energy difference with respect to $\vartheta = \pm\pi/2$ decreases from 1.5 meV to 0.5 meV, respectively. Hence, one can anticipate that with increasing temperature considerable fluctuations of ϑ can be expected. We estimate these fluctuations by $\Delta\vartheta^2 = k_B T (\partial^2 F / \partial \vartheta^2)^{-1} \simeq (\pi/5)^2$ and $(\pi/3)^2$ for 10 and 100 K respectively. Certainly, the proposed spin-orbital ordered state as depicted in Fig. 3 will be destabilized at high temperatures. However, the splitting of the highest-lying doublet remains almost un-

changed across the Neel temperature,¹³ and it is reasonable to expect the exchange splitting of $\varepsilon_{3,5}$ to survive as well, even though the exchange parameters might be somewhat reduced. We would like to mention that the value $\varepsilon_5 - \varepsilon_1 = 31$ meV corresponds nicely to the optical excitation observed for $T > 80$ K, but given the strong fluctuations expected for this temperature range the interval $(\varepsilon_3 + \varepsilon_5)/2 - (\varepsilon_2 + \varepsilon_1)/2 \sim 29$ meV might provide a more suitable estimation of the high-temperature optical excitation.

In summary, we calculated the level-scheme for the energy levels of the vanadium ions and propose an alternating spin-orbital ordering with almost muted magnetic moment as the ground state for Sr_2VO_4 . The proposed scenario and parameter values allow to obtain a consistent picture of the low-temperature excitation spectrum of Sr_2VO_4 , which was recently reported by neutron and optical experiments.

We thank G. Jackeli, D.I. Khomskii, and H.-A. Krug von Nidda for stimulating discussions. This work is partially supported by the SNSF and the National Center of Competence in Research (NCCR) MaNEP and by the DFG via the Collaborative Research Center TRR 80 (Augsburg-Munich). MVE acknowledges support by Ministry Education of the Russian Federation via Grant No. 1.83.11.

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 - ²³ Note that the orbital mixing angle ϑ used in our approach is different from the notation introduced in Ref.12.